REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
11-30-2012

2. REPORT TYPE
FINAL

3. DATES COVERED *(From - To)*
12-1-2011 to 11-30-2012

4. TITLE AND SUBTITLE
Study of Electromagnetic Wave Absorption Properties of Carbon Nanotubes-Based Composites

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-09-1-0367

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Guang-Lin Zhao, PI/PD, Ph. D.,

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Southern University and A & M College, Baton Rouge, Louisiana 70813

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR
875 N RANDOLPH ST
ARLINGTON, VA 22203
DR. CHARLES LEE/RSA

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-OSR-VA-TR-2012-1232

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution A- Approved for public release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
During the period from 12/1/2011 to 11/30/2012, this research project mainly focused on the following three major tasks. These include (1) establishing a broadband electromagnetic (EM) wave absorption properties measurement system for a frequency region from 100 MHz to 20 GHz; (2) fabrications of multiwalled carbon nanotubes (MWCNTs)-epoxy composites samples for EM wave properties measurements; and (3) studies of broadband EM wave absorption properties of the CNT-polymer composite samples, by utilizing the newly established measurement system. We fabricated multi-walled carbon nanotubes (MWCNTs)-epoxy composite samples, using MWCNTs with an average outer diameter (OD) less than 8 nm. The weight fraction of MWCNTs in the CNT-epoxy composite samples was controlled as 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10wt %. We successfully measured the complex permittivity ε and permeability μ, which are the fundamental physical quantities. We have also developed a new method to calculate the absorption ratio of the MWCNTs-epoxy composite samples in the first time in the research. We further analyzed the absorption properties of

15. SUBJECT TERMS
Carbon nanotubes polymer composites;
Electromagnetic wave absorption.

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	U	7	Guang-Lin Zhao, Ph. D., PI

19b. TELEPHONE NUMBER *(Include area code)*
225-771-4491

Reset

INSTRUCTIONS FOR COMPLETING SF 298

1. REPORT DATE. Full publication date, including day, month, if available. Must cite at least the year and be Year 2000 compliant, e.g. 30-06-1998; xx-06-1998; xx-xx-1998.

2. REPORT TYPE. State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.

3. DATES COVERED. Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.

4. TITLE. Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.

5a. CONTRACT NUMBER. Enter all contract numbers as they appear in the report, e.g. F33615-86-C-5169.

5b. GRANT NUMBER. Enter all grant numbers as they appear in the report, e.g. AFOSR-82-1234.

5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. 61101A.

5d. PROJECT NUMBER. Enter all project numbers as they appear in the report, e.g. 1F665702D1257; ILIR.

5e. TASK NUMBER. Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.

5f. WORK UNIT NUMBER. Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.

6. AUTHOR(S). Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, J, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES). Self-explanatory.

8. PERFORMING ORGANIZATION REPORT NUMBER. Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES). Enter the name and address of the organization(s) financially responsible for and monitoring the work.

10. SPONSOR/MONITOR'S ACRONYM(S). Enter, if available, e.g. BRL, ARDEC, NADC.

11. SPONSOR/MONITOR'S REPORT NUMBER(S). Enter report number as assigned by the sponsoring/ monitoring agency, if available, e.g. BRL-TR-829; -215.

12. DISTRIBUTION/AVAILABILITY STATEMENT. Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/ restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.

13. SUPPLEMENTARY NOTES. Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.

14. ABSTRACT. A brief (approximately 200 words) factual summary of the most significant information.

15. SUBJECT TERMS. Key words or phrases identifying major concepts in the report.

16. SECURITY CLASSIFICATION. Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.

17. LIMITATION OF ABSTRACT. This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

To: **technicalreports@afosr.af.mil**

Subject: Final Technical Report to
Dr. Charles Lee, AFOSR/NA, (703)696-7779, charles.lee@afosr.af.mil

Contract/Grant Title: Study of Electromagnetic Wave Absorption Properties of Carbon Nanotubes-Based Composites.

Contract/Grant #: FA9550-09-1-0367.

Reporting Period: December 1, 2011 – November 30, 2012

Principal Investigator (PI): Guang-Lin Zhao, PI/PD, Ph. D., Southern University and A & M College, Baton Rouge, Louisiana 70813.
(Email) Guang-Lin_Zhao@subr.edu; (Phone) 225-771-4491.

Report Date: November 29, 2012

ABSTRACT

During the period from 12/1/2011 to 11/30/2012, this research project mainly focused on the following three major tasks. These include (1) establishing a broadband electromagnetic (EM) wave absorption properties measurement system for a frequency region from 100 MHz to 20 GHz; (2) fabrications of multiwalled carbon nanotubes (MWCNTs)-epoxy composites samples for EM wave properties measurements; and (3) studies of broadband EM wave absorption properties of the CNT-polymer composite samples, by utilizing the newly established measurement system. We fabricated multi-walled carbon nanotubes (MWCNTs)-epoxy composite samples, using MWCNTs with an average outer diameter (OD) less than 8 nm. The weight fraction of MWCNTs in the CNT-epoxy composite samples was controlled as 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10wt %. We utilized an Agilent Vector Network Analyzer N5230C, coaxial transmission method, and Agilent 85071 material measurement software to study the EM wave absorption properties of the CNT-epoxy composite samples for a frequency range from 2 to 20 GHz. We successfully measured the complex permittivity ε and permeability μ, which are the fundamental physical quantities. We have also developed a new method to calculate the absorption ratio of the MWCNTs-epoxy composite samples in the first time in the research. We further analyzed the absorption properties of MWCNTs-epoxy composite samples.

I. Status Quo

Less weight, excellent mechanical, thermal, and electronic properties of carbon nanotubes (CNTs) can be utilized for various applications. Especially, carbon nanotubes - polymer composites can be used for shielding electronic devices against electromagnetic interference, for dampening microwave cavity resonance, and other applications in serving the research interest of the Air Force Office of Scientific Research (AFOSR). The focus of this research project is on utilizing the unusual properties of carbon nanotubes (CNTs) to create new hybrid and multifunctional CNT-polymer composites. In this project, we study the electromagnetic wave, both electric and magnetic, absorption properties of carbon nanotubes (CNTs) based polymer composites. One of the major tasks during this project period is the establishment of a broadband EM wave absorption properties measurement system for a frequency region from 100 MHz to 20 GHz at Southern University and A & M College. Other technical tasks in this period of the project are on (1) fabrications of multiwalled carbon nanotubes (MWCNTs)-epoxy composites samples for broadband EM wave absorption properties measurement system; and (2) measurements of broadband EM wave absorption properties by utilizing the newly established measurement system.

II. Participants

The participants in the research project include Dr. Guang-Lin Zhao (PI), Dr. Jin Tong Wang, postdoctoral research associates (Dr. Zhou Wang and Dr. Guodong Wei), Dr. Yi Zhen (female, assistant professor at Southern University), graduate student (Mr. Cheng Guo), and minority undergraduate students (Desmond Fernandez, Robert Florida, and Juan Arredondo). The project provided research training and mentoring for minority undergraduate students (Desmond Fernondez and Robert Florida) at Southern University and A & M College. The research project has also offered the research training opportunity and research experience for minority undergraduate student Juan Arredondo of Coe College in Iowa from June 1 to July 31, 2012, under the supervising of Dr. Guang-Lin Zhao.

III. Project Activities and New Insights

3.1 Establishing a Broadband Electromagnetic Wave Absorption Properties Measurement System

During this project period, the researchers of this project worked to establish a broadband electromagnetic wave absorption properties measurement system for a frequency region from 100 MHz to 20 GHz at Southern University and A & M College. We acquired a Agilent Technology N5230C PNA-L vector network analyzer, 10 MHz to 40 GHz, a transmission line materials measurement method (1 to 20 GHz), and Agilent Technology 85071E Material measurement software. The transmission line uses a section of coaxial airline. The transmission line method is designed for the measurements of small-size circular samples (3.5 mm in diameter and 1 to 10 mm in thickness). The transmission line method along with Agilent Technology 85071E Material measurement software can measure reflection and transmission coefficients, the effective complex dielectric permittivity and magnetic permeability of the CNT-polymer composite samples, for a continuous frequency range from 2 to 20 GHz. We further developed a new method in research to obtain the absorption coefficients of the CNT-polymer composite samples, utilizing the measured reflection and transmission coefficients and Agilent N5230C PNA-L vector network analyzer. At present, we are also working to establish waveguide fixtures which can extend the measurements from 20 to 40 GHz frequencies, using Agilent N5230C.

3.2 CNT-Composite Sample Preparation

Multi-walled carbon nanotubes (MWCNTs)-epoxy composites were fabricated via mechanical mixture methods. The MWCNTs were obtained from Cheaptubes Company. The purity of CNTs is 99.5%. The outer diameter (OD) of MWCNTs is less than 8nm. The weight fraction of MWCNTs in the CNT-epoxy composite samples was controlled as 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10wt %. Firstly, the epoxy resin and MWCNTs were mixed and stirred in a hotplate magnetic stirrer at 90°C for 1h. Then a hardener was added into the mixture and stirred for 10min. Care was taken to avoid introducing of bubbles in the mixture by controlling the stirring rate. The mixture was then injected in molds and subsequently transferred to the oven for pre-curing and post-curing at 80 and 120 Celsius, respectively. Both of the curing times were 1h.

3.3 Measurements

The EM wave absorption properties of the CNT-epoxy composite samples were measured by utilizing Agilent N5230C PNA network analyzer and coaxial transmission line method for a frequency range from 2 to 20 GHz. The EM wave absorption properties of MWCNTs-epoxy composites are determined by many factors, including the length, width, chirality, conductivity, and outer diameters of MWCNTs as well as the dispersion and distribution of MWCNTs in the epoxy host matrix. The EM wave absorption properties can be described in terms of relative complex permittivity ε and permeability μ, which are the fundamental physical quantities. In this work, the relative complex permittivity ε and permeability μ of the CNT-epoxy samples were calculated by using the S-parameter data from the Agilent N5230C PNA network analyzer and Agilent Technology 85071E Material measurement software.

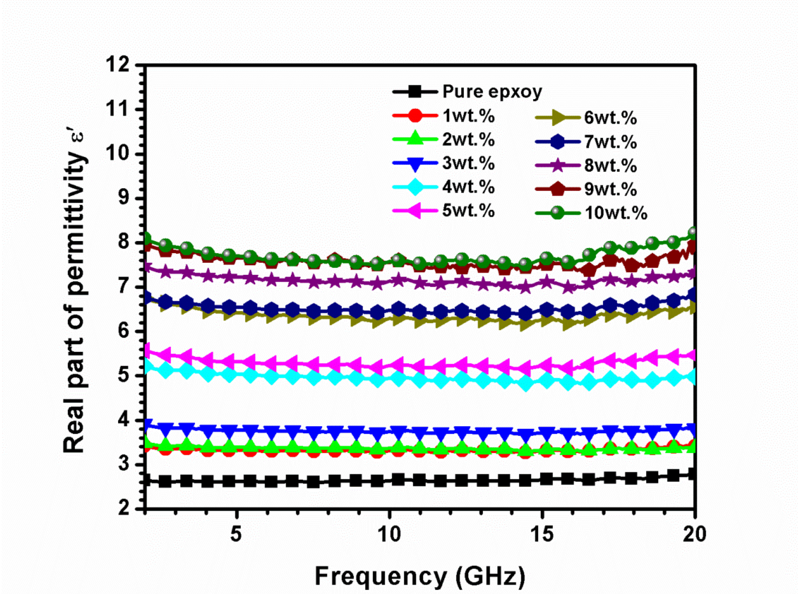

Figure 1. The real part of permittivity ε′ of CNT-epoxy composite samples with different MWCNT weight percentages.

Figure 1 shows the real part of permittivity ε′ of several CNT-epoxy samples with different MWCNT (OD<8nm) weight percentages in the samples. The real part of permittivity ε′ showed a slow increase from about 3 to about 4, when the MWCNT weight percentage increased from 1 to 3wt% in the samples. When the sample has 7 wt%

of MWCNTs in the composite, its real part of permittivity ε′ increased to about 6.5. Further increasing MWCNTs in the polymer composites, ε′ gradually increased to about 8 for the sample with 10wt.% of MWCNTs in the composite.

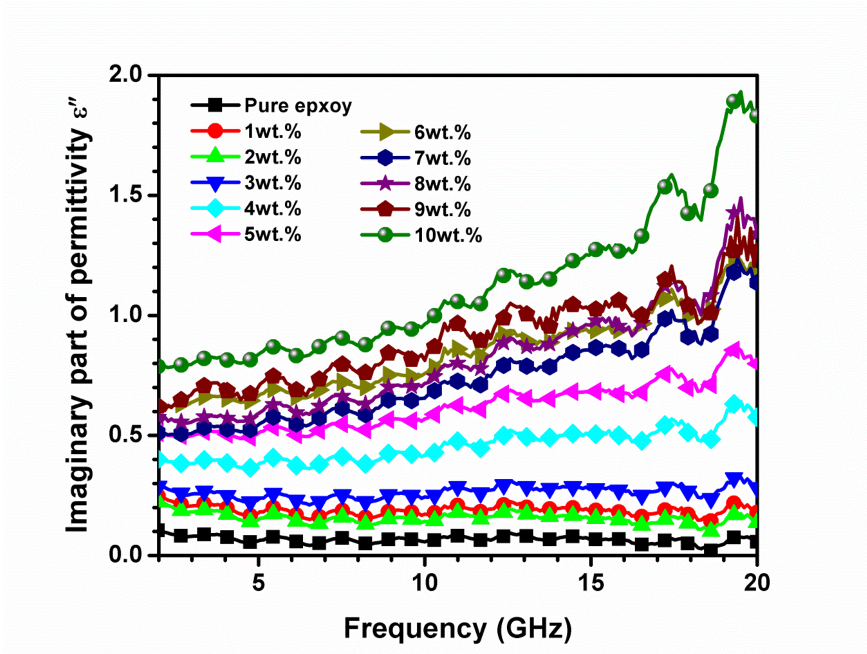

Figure 2. The imaginary part of permittivity ε″ of MWCNT-epoxy composites with different CNTs weight percentages.

Figure 2 shows the imaginary part of permittivity ε″ of the composite samples. For low CNT weight percentages (e.g., from 1 to 3.0 wt % CNTs) in the samples, ε″ varies in a narrow range (from about 0.1 to 0.2) for the frequency range from 2 to 20 GHz). However, for the samples with CNT weight percentages higher than 5 wt%, ε″ increased substantially and showed a frequency dependent behavior, especially for high frequency region from 10 to 20GHz. Generally, the real part of relative complex permittivity ε′ is a measure of how much energy from an external electromagnetic field can be stored in the material, which is due to the electric polarization of the sample. The imaginary part of relative complex permittivity ε″ in the sample represents the dissipative and/or lossy properties to external electromagnetic field. So that, ε″ is a direct measure of microwave absorption properties of the material. Herein, our results clearly showed that the abilities of the sample in the energy storage and electromagnetic wave absorption are substantially improved by increasing the MWCNTs loading fractions in the composites.

The complex permeability μ is a measure of the magnetic interaction of the sample with electromagnetic wave. Due to the weak magnetism of both MWCNTs and epoxy resin, the composite samples showed relatively low permeability, where the real part of permeability μ' fall into the range from 1.1 to 1.4, and the imaginary part of permeability μ'' remained at the value of ~0.8 (Fig. 3). The low values of permeability of the composites show that the microwave absorption of the MWCNTS-epoxy composites was mainly attributed to the dielectric loss.

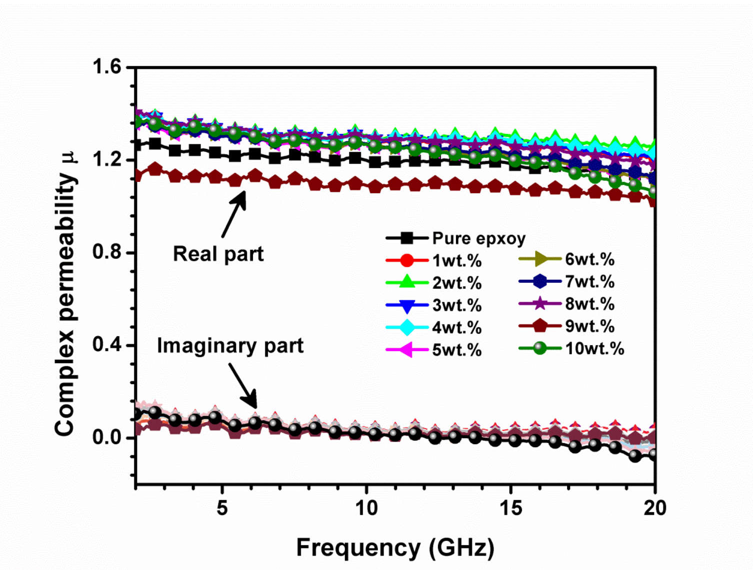

Figure 3. Real and Imaginary part of permeability μ′ of MWCNTs-epoxy composites with different MWCNTs weight percentages.

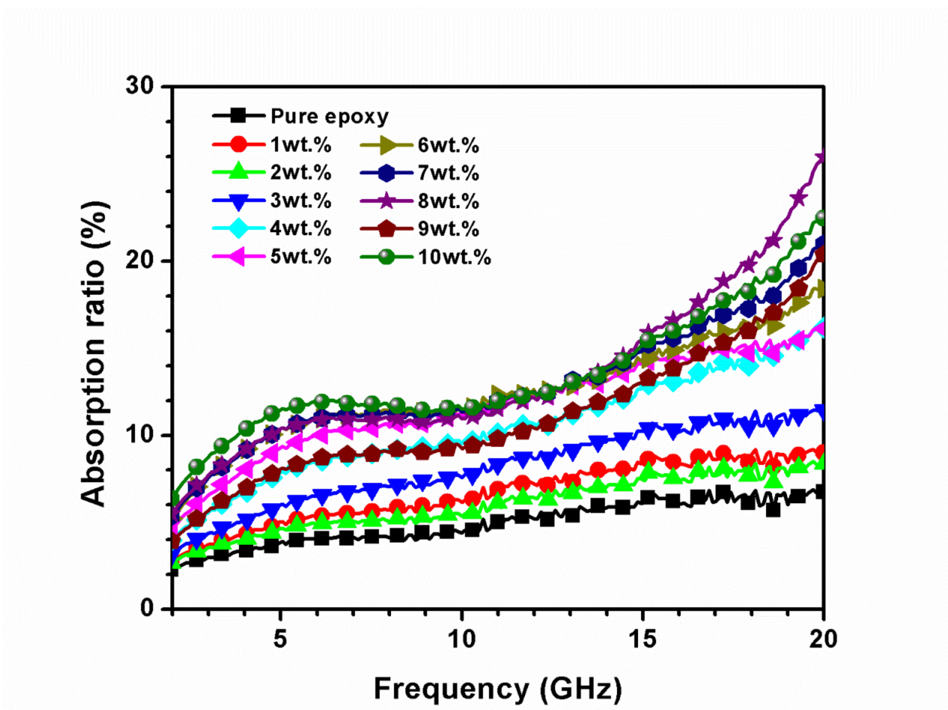

Figure 4. Absorption ratio of MWCNTs-epoxy composite samples with different MWCNTs weight percentages.

When the electromagnetic wave incidents onto the material surface, the interaction between the material and the electromagnetic wave leads to reflection, absorption, and transmission. In this work, we more focused on the electromagnetic absorption properties of the MWCNTs-epoxy composite samples. We have established a new method to calculate the absorption ratio (or coefficient) of the composite samples from the measured S-parameters by utilizing Agilent N5230C PNA-L vector network analyzer. Figure 4 shows the results of the microwave absorption ratio of the CNT-epoxy composite samples for various MWCNT loading percentages in the samples. The absorption ratios of the composite samples increase gradually as the frequency increases from 2 to 20GHz. For the low CNT percentage (1-2wt%) in the samples, the absorption ratio remained low (from 3 to 6%). For the high CNT percentages in the composite samples, the absorption ratios increased substantially. For the composite sample with 8 wt% CNT in the epoxy matrix, the absorption ratio increased from about 6% at 2 GHz to about 23% at 20 GHz. Furthermore, the absorption ratio of the CNT-epoxy composite samples increases significantly when the CNT weight fraction in the composites increases from 3 to 7 wt.%, indicating a significant absorption enhancement to the electromagnetic wave from the samples. This feature is consistent with the results of complex permittivity discussed above.

IV. Significance and Current Impact

In this period of the research project, we have established a broadband electromagnetic wave absorption properties measurement system for a continuous frequency region from 2 to 20 GHz. We acquired a Agilent Technology N5230C PNA-L vector network analyzer, a transmission line materials measurement method (100 MHz to 20 GHz), and Agilent Technology 85071E Material measurement software. We have successfully utilized the new measurement system to obtain the electromagnetic absorption properties of the CNT-epoxy composite samples for a continuous frequency range from 2 to 20 GHz. We have obtained in the first time in research the absorption ratio of the MWCNTs-epoxy composite samples to microwave radiation. We further analyzed the absorption properties of the MWCNTs-epoxy composite samples. In the previous periods of the research work, we utilized a microwave resonant cavity technique to perform the measurements at the University of North Texas, which requires different sizes of the microwave resonant cavities for each measurement frequencies, that is very time consuming to complete the measurements of the samples at various frequencies. The newly established broadband electromagnetic wave measurement system is much more efficient in performing the research tasks required for this research project.

Significant Publications:

[1]. G. L. Zhao, Z. Ye, Z. Li, J. A. Roberts, "New carbon nanotube-epoxy composite for dampening microwave cavity resonance", IEEE Xplore Nanotechnology (IEEE-NANO), 2012 12th IEEE Conference on 20-23 Aug. 2012.

[2]. Z. Li, G. L. Zhao, P. Zhang, S. Guo, J. Tang, " Thermoelectric Performance of Micro/Nano-Structured Bismuth-Antimony-Telluride Bulk from Low Cost Mechanical Alloying", accepted for publish in Materials Sciences and Applications, December 2012 (Vol. 3 No. 12).

[3]. Zhou Wang and Guang-Lin Zhao, "Microwave absorption properties of multi-walled carbon nanotubes - epoxy composites for a frequency range of 2 - 20GHz", a manuscript prepared for publication, November 2012.

[4]. Z. Li, Z. Ye , J. A. Roberts, and G. L. Zhao, “Measurements of Electromagnetic Wave Absorption Properties of Carbon Nanotubes-Epoxy Composites at Microwave Frequencies around 8.43GHz”, Journal of Applied Physics, **110**, 074107 (2011).
[5]. S. Yang, G. L. Zhao, and E. Khosravi, (2011). “Dioxygen adsorption and dissociation on nitrogen doped carbon nanotubes from first principles simulation”, Carbon Nanotubes - From Research to Applications, Chapter 2, pp27 ~ 36. Stefano Bianco (Ed.), ISBN: 978-953-307-500-6, InTech Publisher. Available from:
http://www.intechopen.com/articles/show/title/dioxygen-adsorption-and-dissociation-on-nitrogen-doped-carbon-nanotubes-from-first-principles-simula
[6]. Z. Ye, Z. Li, J.A. Roberts, G.L. Zhao, “Studies of Microwave Absorption Properties of Carbon Nanotubes-Epoxy Composites”, Bulletin of the American Physical Society, Volume 56, Number 1 (2011).

V. Planned Impact

In the next period of the research project, we aim to establish a wave guide method, using Agilent N5230C PNA-L vector network analyzer. The waveguide fixtures can extend the measurement to the frequency region from 20 to 40 GHz. This method can measure the reflection and transmission coefficients, the effective complex dielectric permittivity and magnetic permeability of the CNT composite samples, for a continuous frequency range from 20 to 40 GHz. In addition, we will work to impregnate MWCNTS with iron or nickel nanoparticles, with an aim to provide an enhanced electromagnetic wave absorption through magnetic dipole oscillation in the magnetic field of EM waves. The magnetic iron/nickel nanoparticles mainly provide the magnetic loss of EM waves in relatively low frequency region (low GHz region).

VI. Research Goals

- Development new and high-efficiency EM wave absorbers based on the CNT polymer composites.
- Understanding the electromagnetic wave absorption properties of CNT-polymer composites.

Changes in research objectives, if any: None

Change in AFOSR program manager, if any: None

Extensions granted or milestones slipped, if any: None

Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none): Yes, include new discoveries.